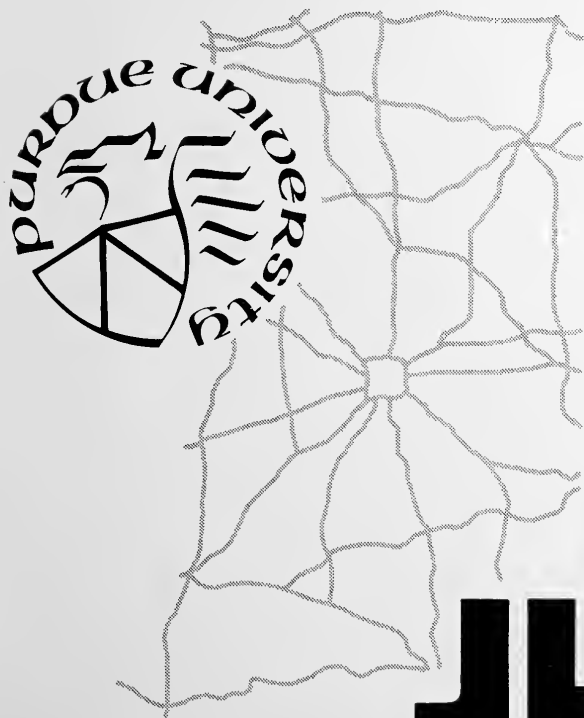


KINETICS OF CALCITE DISSOLUTION

SEPTEMBER 1973 — NUMBER 21



BY

L.C. MUSZYNSKI

JHRP

JOINT HIGHWAY RESEARCH PROJECT
PURDUE UNIVERSITY AND
INDIANA STATE HIGHWAY COMMISSION

Final Report
KINETICS OF CALCITE DISSOLUTION

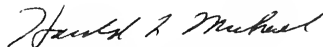
TO: J. F. McLaughlin, Director September 14, 1973
Joint Highway Research Project
FROM: H. L. Michael, Associate Director Project: C-36-47M
Joint Highway Research Project File: 4-6-13

The attached Final Report titled "Kinetics of Calcite Dissolution" is on the approved J.H.R.P. Research Study of the same title. It has been authored by Mr. Larry C. Muszynski, Graduate Assistant in Research on our staff under the direction of Professor W. L. Dolch.

The objective of the Study was to investigate the influence of retarders, both proprietary substances and pure chemicals, on the rate of dissolution of calcite by dilute HCl. Findings included that admixtures decreased the reaction velocities and the rate constants and that activation energies were generally increased.

The Report is submitted to the Board for acceptance as fulfillment of the objectives of the Study.

Respectfully submitted,



Harold L. Michael
Associate Director

HLM:ms

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Final Report
KINETICS OF CALCITE DISSOLUTION

by
Larry C. Muszynski

Joint Highway Research Project

Project No.: C-36-47M

File No.: 4-6-13

Conducted by
Joint Highway Research Project
Engineering Experiment Station
Purdue University
In Cooperation with
Indiana State Highway Commission

Purdue University
West Lafayette, Indiana
September 14, 1973

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The Author wishes to express his appreciation to his major professor, Dr. W. L. Dolch, for his active participation, guidance, and understanding during the course of this work. The valuable suggestions and technical advice of Dr. S. Diamond are gratefully acknowledged.

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ABSTRACT

Muszynski, Larry Chester. M.S., Purdue University, August 1973. Kinetics of Calcite Dissolution. Major Professor: Dr. W. L. Dolch.

The kinetics of the dissolution of calcite in dilute hydrochloric acid (0.0184 - 0.0364 M) were studied at these temperatures, 15°C, 25°C, and 35°C. Velocities, rate constants, and activation energies were determined. The influence of various substances, including proprietary retarders and other reagents that are influential in controlling the rate of setting of portland cement were studied. In the absence of admixtures the rate constant was 1.99×10^{-6} lit/sec-cm², and the activation energy was 5.33 kcal/mole.

Admixtures, and especially the commercial retarders, decreased the reaction velocities and rate constants. The activation energies were generally increased, in some instances greatly, to a maximum of 13.2 kcal/mole. The pre-exponential factors in the Arrhenius equation were also greatly changed in some instances. It is concluded that the presence of the proprietary retarders can cause a change in the nature of the rate-determining step of the reaction studied.

INTRODUCTION

Any material other than water, aggregate, and hydraulic cement that is used as an ingredient of a concrete mixture and is added immediately before or during its mixing is defined as an admixture. This excludes materials interground or interblended with the hydraulic cement. An admixture is used to make the concrete more suitable for the purpose for which it is made or to reduce its cost.

One important class of admixtures is retarders, which are used principally to delay the setting time, although they bring about other beneficial changes as well. Retarders can compensate for adverse conditions, particularly in hot weather concreting. Retarders are in increasingly common use and are being used presently in 50 to 60 million cubic yards of concrete per year.

Commercial retarders are usually classified into three chemical categories:

- 1) lignosulfonic acids and their salts,
- 2) hydroxycarboxylic acids and their salts,
- 3) carbohydrates (sugars).

Their mode of action is largely unknown. Their retarding action is said to be due to some kind of physical and/or

chemical reaction. One possible effect is a change in the kinetics of the cement hydration reactions. Other theories of retardation postulate physical changes, such as the formation of a "coating" on the cement grains to protect them from attack by the water, or some change in the morphology of the hydration products. But these theories do not exclude a possible change in the kinetics of the reaction itself.

So the retardation can be explained, at least partly, by a rate change or a change in the activation energy of the process. The activation energy is the energy that a molecule must possess before it can react with another molecule upon collision, and is a basic parameter of chemical kinetics.

The hydration of portland cement involves complex simultaneous and competing reactions of several components of the cement with water. The so-called "through-solution" hypothesis implies that the dissolution of these components is a major step in the hydration process. For the compounds β -C₂S and γ -C₂S*, there is an indication (1) that the rate-determining step in the hydration is the protonation of the surface silicate ion of the anhydrous solids.

* In this report the conventional shorthand of cement chemistry is used: C= CaO, S= SiO₂, A= Al₂O₃, F= Fe₂O₃, H= H₂O, etc.

The aim of the present work, therefore, was to study a reaction that is simpler but is thought to proceed by the same mechanism as the cement hydration, and that has been studied comparatively thoroughly. The effects of retarding admixtures on the rate of such a "model" reaction could be determined and applied by analogy toward the more complex cement hydration system.

A simple, first order, heterogeneous, chemically-controlled reaction, whose rate-determining step is thought to be the same as that of the cement hydration reaction, that is, protonation of the surface oxygens, is the dissolution of calcite (CaCO_3) by dilute strong acids.

The present paper discusses the results of experiments undertaken to gain information concerning the influence of retarders, both proprietary substances and pure chemicals, on the rate of dissolution of calcite by dilute HCl.

LITERATURE REVIEW

Chemical reactions proceed at a rate that is a function primarily of the concentration of the reactants and the temperature. The determination of the extent of reaction as a function of time, concentration of species present and temperature permits, in principle, the calculation of the rate constants and the activation energy of the process (2). The latter, in turn, is indicative of the molecular mechanisms that are taking place. Such determinations are complicated by competing reactions, sequential reactions, and physical rate processes such as diffusion phenomena. In the case of sequential reactions, the slowest step is rate-controlling, and the calculated activation energy is indicative of the mechanism of this slowest reaction.

The mechanism of the hydration of cement is largely unknown, primarily because several reactions are taking place simultaneously and sequentially and because molecular diffusion may play an important role. The state of knowledge is reviewed by Kondo and Ueda (3). The kinetics of the hydration of alkaline-earth orthosilicates were studied by Campbell (1) who postulated that a rate-determining step for β -C₂S and γ -C₂S is the protonation of a surface silicate ion in the solid, or more specifically, the oxygen atoms. Weyl (4)

has postulated the same sort of mechanism for the dissolution of carbonates such as calcite and magnesite by dilute acids.

The rate constants for the dissolution of calcite have been reported by several workers whose results were summarized by Moelwyn-Hughes (5). These early results have been confirmed by Bassow et. al. (6), who obtained an activation energy of 6.4 kcal/mole for the $\text{CaCO}_3\text{-HCl}$ reaction. Tominga, Adzumi, and Isobe (7) corrected for the fact that the viscosity of the solution decreases as the temperature increases, thus increasing the velocity of the reaction which they claimed to be inversely proportional to the viscosity of the solution. This correction gave a value for the activation energy of 5.4 kcal/mole. These workers studied systems that were stirred rapidly to eliminate the effects of diffusional barriers. Whether the objective was achieved by their method of stirring is conjectural.

Spring (8) was the first to establish that the rate of dissolution of marble by dilute acids is unimolecular. Brunner (9) showed that marble dissolves faster in strong acids than does magnesite. Palmaer (10) found that Iceland Spar, another form of calcite, was not as suitable as marble because of the many minute fissures found in the surface after cleavage fracture of the crystals, thus

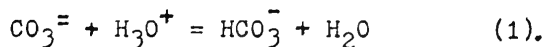
yielding different velocities of CO_2 evolution for different crystallographic faces of the crystal.

King and Liu (11) supported the diffusion theory as applied to the rate of dissolution of calcite in dilute acids. The diffusion theory holds that the rate-determining step is either the diffusion of the products from the surface of the solid to the bulk solution or, as the Nearnst theory contends, the diffusion of the solute to the solid surface. They also contended that additives, such as sucrose, affect the reaction rate by increasing the viscosity of the solution and thus changing the diffusion rates.

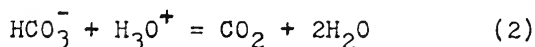
Tominga, Adzumi, and Isobe (7) claimed that the chemical reaction is rapid at the solid surface, and that the reaction follows Nearnst's theory of diffusion of the solute through the product layer. Moelwyn-Hughes (5) pointed out that the diffusion theory fails to explain why calcite dissolves much faster in dilute HCl than magnesite or dolomite. Also it would be reasonable to expect marble and Iceland Spar to dissolve at the same rate if diffusion governs the rate process, which according to Palmaer (10) is not the case. Moelwyn-Hughes (2) also pointed out the illogic of applying, to reactions carried out with violent stirring, the diffusion coefficient determined in unstirred solutions. Centnerszwer and

Heller (12) concluded that at high stirring speeds the acid reaches the surface of the solid faster than it can react, and the diffusion layer consequently disappears. Barrow et. al. (6) claimed that low HCl concentration ($\sim 0.05M$), fast stirring speeds (~ 900 r.p.m.), small particle size (~ 20 mesh), and low temperature ($\sim 35.0^\circ C$) all tend toward a chemically controlled reaction.

The reaction in question consists of the removal of carbonate ions from the crystal, presumably



The subsequent decomposition of the bicarbonate ion



is thought to be rapid, so that reaction (1) is rate-controlling. According to this mechanism one molecule of CO_2 is produced for each hydrogen ion that disappears as a result of colliding and reacting with the solid surface and the reaction is thereby unimolecular.

EXPERIMENTAL WORK

Materials

Marble chips were used as the calcite. They were ground in a mortar and pestle, sieved between the No. 16 and No. 30 sieves, washed with distilled water on the sieve, and oven-dried on the sieve at 110°C . After drying, the crushed marble was sieved again, washed again, re-dried, and bottled.

The calcium and magnesium contents of the marble were determined by dissolution in HCl and complexometric titration in the usual way. The result, for the marble from Fisher Chemical Co., was 99.25% CaCO_3 , and 0.39% MgCO_3 .

Dilute HCl was made up in 5 gallon carboys and standardized against Na_2CO_3 , using methyl red. The standardizations yielded acid strengths of 0.0184M, 0.0274M, and 0.0364M.

The admixtures used were:

Citric Acid monohydrate, reagent grade.

Sucrose, reagent grade.

Glycerol, purified grade.

Calcium Chloride, reagent grade.

Calcium Di-noculfonate, supplied courtesy of V. Dodson

Three proprietary retarders, each representing one of the three major classes of these materials, were used. They are referred to by code letters as follows (Table 1).

Table 1

Proprietary Retarders

Code Letter	Type	Density, g/cc.	Solids Content, wgt, %
L	Lignosulfonate	1.147	32.2
A	Hydroxycarboxylic acid	1.152	32.6
S	Carbohydrate	1.175	35.1

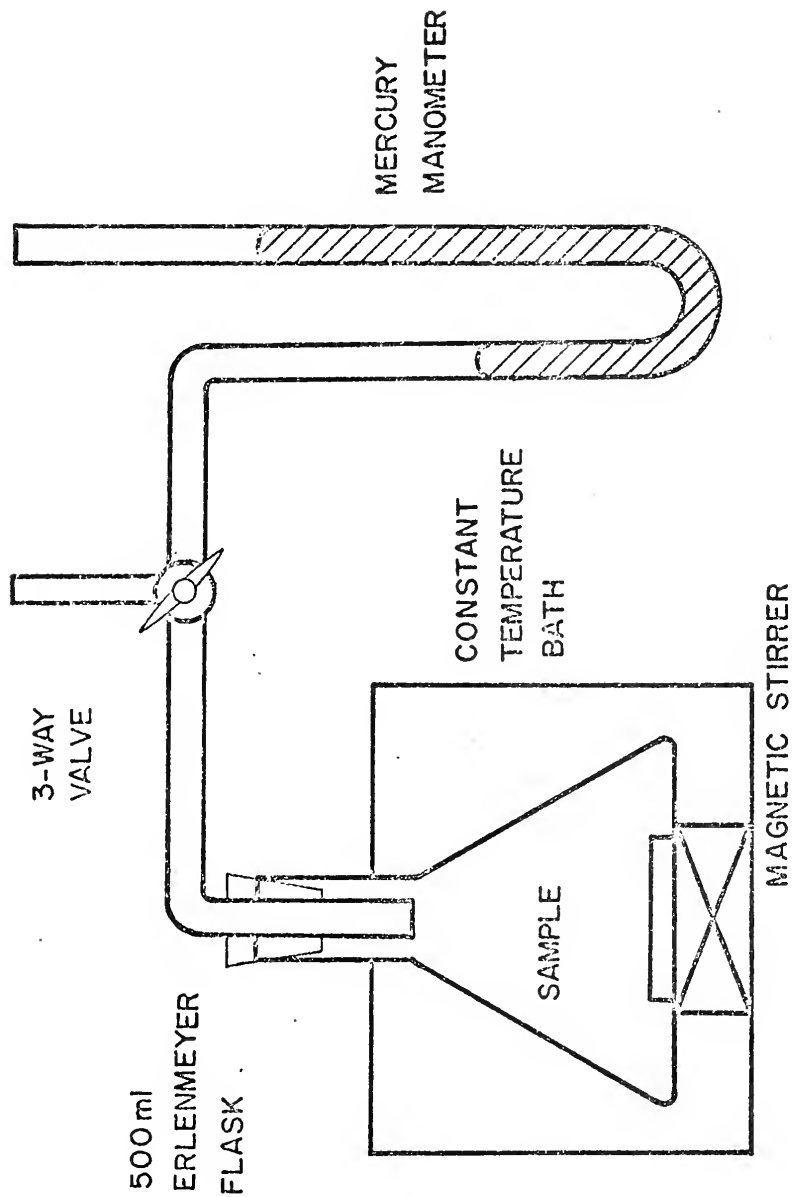
Apparatus & Procedure

The rates of the calcite dissolution reaction were determined by using the apparatus shown in Figure 1.

The reaction flask was immersed in a constant-temperature water bath controlled at temperatures of 15°, 25°, and 35°C \pm 0.01°C.

The reaction flask was stirred internally with a submersible magnetic stirrer (Henry Troemner, Inc.) operating at about 900 rpm.

The reaction flask was connected by Tygon tubing to a three-way stopcock with one side free to the atmosphere

FIG.1 CaCO_3 DISSOLUTION APPARATUS

and the third side attached through another piece of Tygon to a mercury manometer, 6.0 mm i.d. The manometer was read by means of an attached scale.

To start a run, at a specific temperature and HCl concentration, 400 ml of acid were introduced into the flask and stirred for 15-20 minutes to allow the solution to come to temperature equilibrium with the bath. The stopcock was positioned so that both the flask and the manometer were open to the atmosphere.

Then the sample, 2.50 ± 0.01 g of the crushed marble, was added to the flask, the stopper was immediately inserted, and the timer was started.

At this zero of time for the run the system was at atmospheric pressure because of the stopcock position. Immediately then, the stopcock was turned to connect flask and manometer. The time for the accomplishment of these initial operations was only 2 or 3 seconds.

Then as the reaction proceeded its course was followed by taking readings of the pressure change in the manometer as a function of time. Readings were usually taken at intervals of ΔP of five torr. For slower reactions, as with admixtures L and A, readings were taken at intervals of three torr.

The readings were continued to a maximum pressure difference of about 40 torr, but usually it was less.

The run thus corresponded to the consumption of only a few percent of the acid present, as will be shown later (Appendix C).

Duplicate runs were made on the control reaction (i.e., no admixture) but not on those containing the admixture. To a certain extent, of course, the regular program of runs for each solution contained an internal check on reproducibility by the requirement of linearity of the plots from which the activation energies were calculated.

The viscosity of each solution, including those with admixtures, was determined using a falling-ball viscometer with a stainless-steel ball. The estimated accuracy was 1 or 2 percent. The constant for the apparatus was determined by duplicate measurements on water.

Admixture concentrations in the reacting solutions were either 0.25 percent or 1.0 percent (weight of solids in admixture/ volume of reacting acid solution).

DATA

The data from the kinetic measurements are presented in Table (2) as reaction velocities, which are the slopes of plots of pressure change in the reaction flask vs. time. These velocities were determined at three temperatures, 15, 25, and 35°C and at three acid concentrations, 0.0184M, 0.0274M, and 0.0364M.

Table (3) gives a summary of the viscosities of the solution with and without admixtures at the three different temperatures and with an acid concentration of 0.0274M, which is the median concentration of the three used.

Table 2. Summary of Reaction Velocities With and Without Admixtures

Admixture	Conc. of Admixture	Temp. = 15.0°C		Temp. = 25.0°C		Temp. = 35.0°C	
		[HCl] moles/liter		[HCl] moles/liter		[HCl] moles/liter	
(1)	-	0.0184	0.0274	0.0184	0.0274	0.0184	0.0274
(2)	-	0.158	0.248	0.255	0.348	0.358	0.517
AVG.	-	0.152	0.244	0.244	0.342	0.352	0.507
	-	0.155	0.246	0.250	0.345	0.355	0.512
Sucrose	0.25%	0.169	0.222	0.256	0.293	0.306	0.394
Sucrose	1.0%	0.143	0.200	0.270	0.311	0.283	0.400
Citric Acid	0.25%	0.151	0.172	0.198	0.333	0.403	0.490
Ca Ligno-sulfonate	1.0%	0.050	0.078	0.096	0.106	0.120	0.176
Retarder B	1.0%	0.033	0.043	0.051	0.077	0.066	0.120
Retarder A	1.0%	0.034	0.048	0.059	0.090	0.098	0.121
Retarder S	1.0%	0.064	0.105	0.140	0.125	0.102	0.192
Calcium Chloride	1.0%	0.189	0.224	0.294	0.341	0.357	0.476
Glycerol	1.0%	0.181	0.204	0.250	0.333	0.300	0.416

Table 3. Summary of Solution Viscosities and $k\eta/T$ Values for the Temperatures in Question With and Without Admixtures

Admixture	Conc. of Admixture	Density of Soln. g/cc	Temp. = 15.0°C		Temp. = 25.0°C		Temp. = 35.0°C	
			η in centipoises	η in $\frac{\text{cP}}{\text{g}}$	η in centipoises	η in $\frac{\text{cP}}{\text{g}}$	η in centipoises	η in $\frac{\text{cP}}{\text{g}}$
None	-	0.9983	1.18	0.65	0.93	0.43	0.83	0.36
Sucrose	0.25%	0.9980	1.21	0.42	0.91	0.24	0.85	0.25
Sucrose Citric	1.0%	1.0019	1.23	0.66	0.95	0.42	0.85	0.35
Acid Ca Ligno sulfonate	0.25%	0.9997	1.20	0.51	0.92	0.34	0.86	0.24
Retarder	1.0%	1.0006	1.25	0.21	0.97	0.16	0.86	0.11
Retarder A	1.0%	0.9993	1.27	0.09	0.96	0.09	0.88	0.13
Retarder S	1.0%	1.0011	1.27	0.12	0.94	0.08	0.88	0.07
Calcium Chloride	1.0%	1.0035	1.21	0.33	0.95	0.23	0.86	0.22
Chloride	1.0%	1.0007	1.26	0.50	0.96	0.34	0.86	0.31
Glycerol	1.0%	0.9996	1.27	0.39	0.99	0.33	0.93	0.37

DISCUSSION

Pertinent Kinetic Equations

The data were taken in the form of change in pressure in the reaction flask, as read on the manometer, vs. time. The slope of such a plot is the reaction velocity, $v = dp/dt$ in units of torr/sec. These values were presented in Table(2),

When v is plotted as a function of acid concentration at constant temperature the slope of the curve is the apparent rate constant, k' , defined by

$$\frac{dp}{dt} = k' [H^+] \quad (3)$$

and with units of torr-lit/mole-sec. The apparent rate constants are given in Table (4).

The activation energy is determined by plotting the logarithm of the rate constant against reciprocal temperature. The slope of such a plote is the apparent activation energy divided by the gas constant according to

$$k' = A \exp (-E_a/RT) \quad (4)$$

which is the Arrhenius equation. The calculated activation energies are also given in Table (4).

Table 4. Summary of Apparent Rate Constants, Activation Energies, and Frequency Factors for the Calcite Dissolution Reaction With and Without Additives

Admixture	Conc. of Admixture	k', 15.0°C torr-lit mole-sec	k', 25.0°C torr-lit mole-sec	k', 35.0°C torr-lit mole-sec	E kcal/ mole	A lit/ sec-cm ²
None	-	8.21	11.43	15.07	5.33	8.2×10^4
Sucrose	0.25%	5.25	7.00	10.60	5.30	1.2×10^5
Sucrose Citric Acid	1.0%	8.00	11.00	14.50	5.10	5.2×10^4
Ca Lignosulfonate Retarder	0.25%	3.14	6.00	9.14	9.60	5.5×10^7
Retarder	1.0%	2.50	4.00	5.70	7.20	6.9×10^5
Retarder	1.0%	1.10	2.30	5.30	13.2	1.0×10^{10}
Retarder	1.0%	1.42	2.00	2.60	5.30	1.4×10^4
Calcium Chloride	1.0%	4.12	6.18	9.20	7.10	9.3×10^5
Glycerol	1.0%	6.00	8.80	12.60	6.20	2.0×10^5
	1.0%	4.66	8.33	14.00	9.10	3.5×10^7

A complete calculation, including appropriate curves, is given in Appendix A for the control, or no-admixture, data. The method of calculation for the other runs was identical.

Heterogeneous reactions in solution are influenced by the extent of solid surface present. Moelwyn-Hughes (2) gave the rate constant of this dissolution as proportional to the first power of the surface area. Therefore, a true, as opposed to an apparent, rate constant can be defined by

$$\frac{dn_{\text{CO}_2}}{dt} = kS [\text{H}^+] \quad (5)$$

where the rate constant, k , has the dimensions lit./sec-cm^2 or, more generally, cm/sec and n_{CO_2} is the moles of CO_2 evolved during the reaction. The relationship between k and k' is derived in Appendix B. The linear nature of this relationship makes the use of either k or k' a valid route, via the logarithm, for the determination of the activation energy.

Experimental Problems and Assumptions

One problem was the change in the acid concentration of the solution as CO_2 was evolved and acid was used up. An analysis of this matter is given in Appendix C. The results illustrate that the maximum reduction in acid

strength is about 5%, but the effects on the determination of k' are less because all points will be moved in the same direction on the plot of v vs. $[H^+]$ and, therefore, the slope will be little affected.

Another problem concerns the value of specific surface used to determine the total surface area of the marble sample used. The derivation given in Appendix B assumes the particles to be cubes with an edge dimension equal to the algebraic mean of the two sieve sizes. Such a model has obvious deficiencies. The "true" surface area is no doubt larger than the one so calculated, probably by several times, because of surface roughness. But the same problem and relative error was no doubt encountered by others who did similar experiments, so a comparison of these results and theirs on this basis is probably valid.

The reproducibility of the measurements is shown in Table(2) for the control reaction, no admixture, in which duplicate runs of dp/dt yielded a difference of only 2% from the mean value. The k' and E_a values in Table (4) were calculated from the mean values of dp/dt .

Agreement of Results with Those of Other Investigators

When the results of other workers are calculated in terms of equation (5) the following k values, in lit/sec-cm^2 , are obtained: Bassow et. al. (6), 2.31×10^{-6} ;

Tominga et. al. (7), 3.6×10^{-6} ; and King and Liu (11), 2.8×10^{-5} , all at 25°C .

The value obtained in the present work was 1.99×10^{-6} lit/sec-cm² (Appendix B), which agrees reasonably well with the first two values mentioned above, but not with the third, by an order of magnitude. The reason for such a difference is not known.

The activation energies for the control reaction vary somewhat from the results of others. Barrow et. al. obtained a value for E_a of 6.4 ± 0.3 kcal/mole; King and Liu obtained a value of 5.82 ± 0.77 kcal/mole. Tominga et. al. accounted for viscosity effects, that is changing the temperature from 15°C to 35°C decreases the viscosity of the solution, and obtained a value of 5.4 ± 0.2 kcal/mole.

The value obtained in the present work was 5.33 ± 0.3 kcal/mole (Table 4), which agrees with the work of Tominga et. al. and is within the limits of the value determined by King and Liu. The E_a value of Barrow et. al. is an order of magnitude greater than the value obtained in the present work.

Chemical or Diffusion Control

There are several parameters from which one can decide whether a reaction is chemically controlled or diffusion controlled. Moelwyn-Hughes (2,5) illustrates

five such. One is μ , the mobility of the hydrogen ions as they approach the solid surface. This mobility can be calculated from the equation

$$k = \mu \exp (-E_a/RT) \quad (6)$$

Another parameter is δ , the thickness of the (perhaps fictitious) diffusion layer, calculated from the Nernst equation $k_1 = D/\delta$ where D is the coefficient of diffusion. Another test is the influence of temperature on the velocity of the reaction. The coefficient dk/dT should equal dD/dT , and the increment of energy should be 4.5 kcal/mole for a diffusion controlled reaction. This is the differential of the Nernst equation with respect to temperature. Another characteristic of reactions governed by diffusion is that the value of k , the rate constant, varies with stirring speed. Lastly, if the ratio k'/T is constant, the velocity would be diffusion controlled, since in the diffusional process the rate constant shows a linear dependence on temperature, whereas for a chemically controlled process the rate constant is exponentially dependent on the temperature.

From the value of k obtained in the present work, 1.99×10^{-6} lit/sec-cm², the value for the mobility of the hydrogen ions was calculated using 5.33 kcal/mole for the value of E_a . The calculated mobility of the hydrogen ions in the solution was 13.7 cm/sec.

The calculated thickness of the diffusion layer, δ , using the CRC Handbook value for the diffusion coefficient, was 1.5×10^{-2} cm.

The temperature coefficient of the rate constant, dk/dT , had an energy increment of 5.33 kcal/mole, i.e., the activation energy.

The ratio k'/T for the temperatures 15.0°C, 25.0°C, and 35.0°C were given in Table (3) and found not to be constant for the control reaction.

The following conclusions can be drawn from these results. A hydrogen ion mobility of 13.7 cm/sec is too fast to be part of a diffusional process. A layer thickness of 0.15 mm, about 20% of the diameter of the particle, is so large as to border on the physically impossible. The critical increment of energy, 5.33 kcal/mole, is larger than the maximum energy for diffusional reactions, 4.5 kcal/mole. When these figures are converted to the appropriate exponentials the larger represents a rate one fourth that of the smaller.

The above results indicate that, for the conditions used here, the rate of the calcite dissolution is chemically, rather than diffusionally, controlled if no admixture is present.

Effect of Admixtures on the Velocity

In general, both the pure chemical and proprietary retarders reduced the velocity of the reaction, as shown in Table (2). The 0.25% sucrose showed a slight accelerating effect at the low HCl concentrations and low temperatures. CaCl_2 , which is an accelerating admixture for concrete, showed an accelerating effect at low HCl concentrations at any temperature. Glycerine, which has no effect in concrete, behaved as 0.25% sucrose.

Calcium lignosulfonate and the proprietary retarders, L, S, and A retarded the velocity by 60-70%, while the pure chemical retarder, e.g. sucrose, retarded the velocity by only 5-10%. It is perhaps significant that the proprietary retarders had a much greater influence on the reaction velocity than did any of the pure chemical species. Retarder L and Retarder A appear to retard better than Retarder S and purified calcium lignosulfonate. Retarder L reportedly contains lignosulfonate salts plus sugar derivatives.

Reference to Figures 2, 3, and 4 shows that a period of about 20 seconds elapsed before gas evolution began,

as shown by the intercept of the curves on the time axis. This induction period was not greatly affected by any of the admixtures.

Effect of Admixtures on Apparent Rate Constants

The apparent rate constant k' , as stated previously, was obtained from the slopes of the curves of dp/dt , the velocity, vs. the HCl concentration at the three temperatures 15.0°C, 25.0°C, and 35.0°C. The rate constant can be thought of as a measure of the extent of the reaction at unit time and concentration.

It can be noted from Table (4), that the addition of the admixtures result in reduced apparent rate constants. That is, all the admixtures made the dissolution less sensitive to changes in acid concentration. The proprietary retarders and calcium lignosulfonate, again, reduced the apparent rate constant to a much greater degree than did the pure chemical substances.

This near-universal reduction in the rate of the reaction and in its sensitivity to acid by the admixtures, and especially by the proprietary retarders, is probably significant.

Effect of Admixtures on the Activation Energy

The effect of the admixtures on the activation energy of the reaction is shown in Table (4). The values range from 5.1 kcal/mole to 13.2 kcal/mole, and are, in general, larger than the value for the control reaction. The implication of these results is that different processes become rate-controlling when some admixtures are present.

A difficulty is the question of the variability in E_a due to ordinary experimental error. A trial calculation shows a 10 percent error in one of the k' values, most improbably large, to result in a change in E_a of 1 kcal/mole. So any differences in E_a substantially smaller than this can probably not be attributed to differences in mechanism of the slow reaction.

The run with citric acid may be anomalous, because citric is apparently a strong enough acid to dissolve calcite by itself (11). So the result with citric acid may reflect a combined action.

The other E_a values can perhaps be grouped as follows: sucrose, Retarder A, CaCl_2 - about the same as the control reaction; Retarder S and calcium lignosulfonate; glycerine; Retarder L.

If the same molecular process is occurring as the slow and rate-determining step in the reactions, the E_a should be the same. A necessary influence is, therefore,

that those reactions that yielded appreciably higher values of E_a have a different mechanism. What it may be cannot be determined from these data. The fact of a linear $\ln k'$ vs. $1/T$ plot argues for the same process occurring at the various temperatures in question, whatever it may be.

In Table (4) are also given the values of the pre-exponential factor, A , of the Arrhenius equation, $k' = A \exp (-E_a/RT)$. According to the collision theory, A is a factor proportional to the frequency with which reacting species collide with each other. It can be seen that the A factor is greatly influenced by the presence of some admixtures, notably Retarder L. The implication is that the presence of Retarder L, and of glycerine as well, causes an increase in the rate of collision of the reacting molecules.

Campbell (1) found that the activation energies of hydration of β - and γ - Ca_2SiO_4 were 11.4 kcal/mole and 16.1 kcal/mole, respectively. The 5.33 kcal/mole activation energy in the control reaction is much less than the E_a 's measured by Campbell, which can perhaps be accounted for by the different type of anion geometry between a silicate, SiO_4^{4-} , tetrahedron and a trigonal carbonate, CO_3^{2-} , ion. This different geometry and/or the difference in polarizability of the central atom, silicon and carbon respectively, may be responsible for the

difference in the activation energy, for the mechanism of attack of the oxygen surface of the solid by the hydrogen ions of the acid.

Effect of Admixtures on the Ratio $k'\eta/T$

The viscosities of the solutions, with and without admixtures were measured at 15.0°C, 25.0°C, and 35.0°C. The viscosities at the high temperature may be high due to some cooling, but the difference in the $k'\eta/T$ ratio is less than 10% and can be neglected. Table (3) shows that for the retarders the ratios are not equal for the low temperatures, 15.0°C to 25.0°C but become more so for the 25.0°C to 35.0°C range. Calcium lignosulfonate, glycerine, Retarder L, and Retarder A, have fairly constant ratios throughout the entire temperature range, whereas the others are so only in the higher temperature range. The control reaction is not affected by the higher temperatures and thus, according to Moelwyn-Hughes (5), is a chemically controlled reaction, as stated previously. The others, however may tend toward diffusion control at 25.0°C to 35.0°C, based on this criterion.

These results indicate a possible adsorption of the admixture on the solid surface which tends to result in a diffusion controlled reaction, making diffusion of hydrogen ions to the surface or diffusion of products away from the surface, the rate-determining step.

CONCLUSIONS

The following conclusions seem reasonable, and are based on the materials used and the results of the experiments performed.

1. The proprietary substances including calcium lignosulfonate that retard the hydration of portland cement have a strongly inhibiting effect on the dissolution of calcite in dilute hydrochloric acid, as judged by changes in the velocities and rate constants of the reaction. A logical inference is that they do so by similar processes in the two systems.

2. The presence of the retarders, in some instances, causes large changes in the activation energies and the pre-exponential factors. A logical conclusion is that their presence causes different processes to become rate-controlling than those that control the reaction in their absence.

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BIBLIOGRAPHY

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APPENDICES

APPENDIX A

APPENDIX A

Sample Calculation

Figures 2, 3, and 4 give the raw data for the control reaction, no admixture. The reaction velocities were calculated from the slopes of the dp vs. dt plots at three different HCl concentrations 0.0184M, 0.0274M, and 0.0364M, and at three different temperatures 15.0°C, 25.0°C, and 35.0°C.

Figure 5 shows the determination of the apparent rate constants, for the control reaction, at the three temperatures in question. The rate constants are calculated from the slopes of the velocity vs. HCl concentration plots.

The activation energy of the control reaction is calculated from the slope in Figure 6, where the logarithm of the apparent rate constants are plotted against the reciprocal of the absolute temperatures. The slope of the line is equal to $-E_a/R$, where E_a is the activation energy and R is the gas constant.

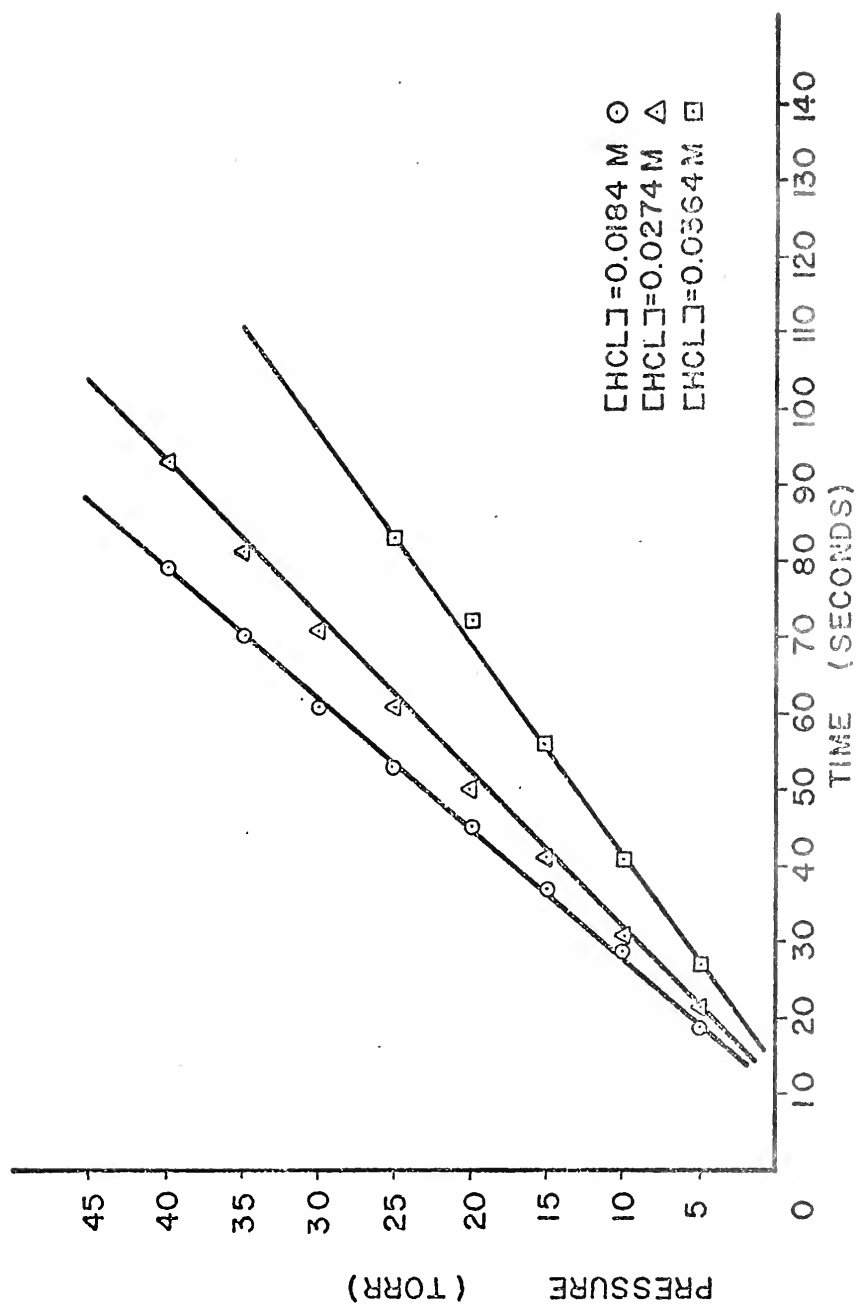


FIG. 2 VELOCITY OF REACTION AT 15.0°C

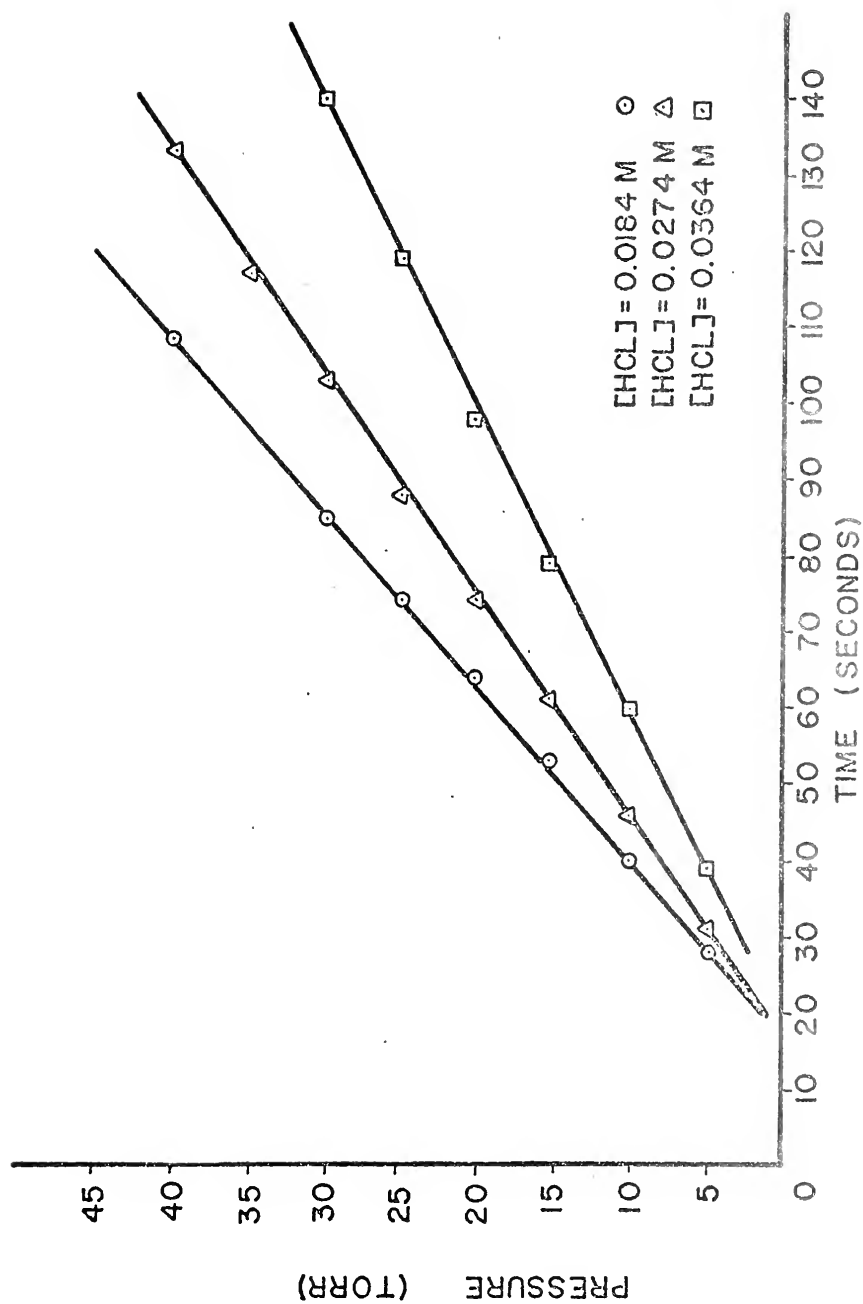


FIG. 3 VELOCITY OF REACTION AT 25.0°C

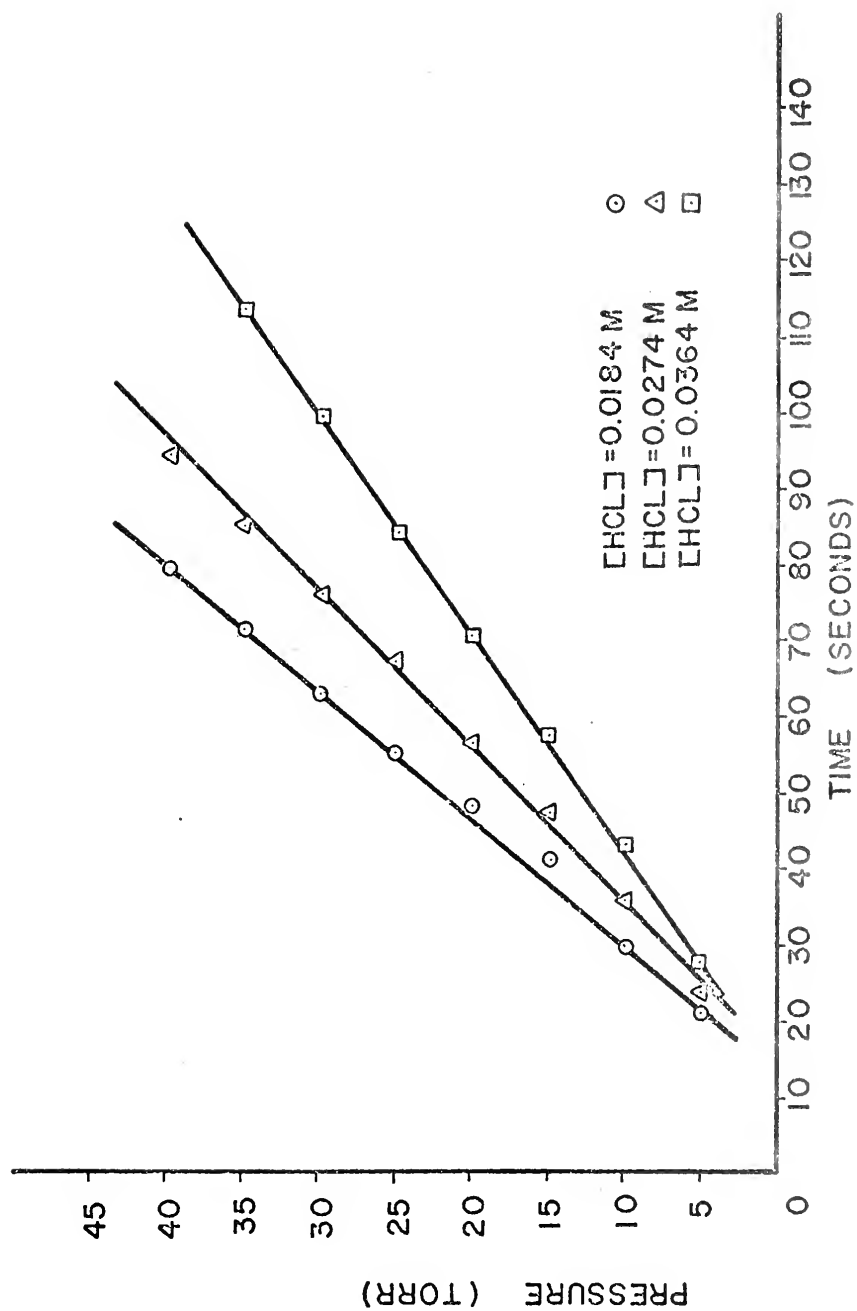
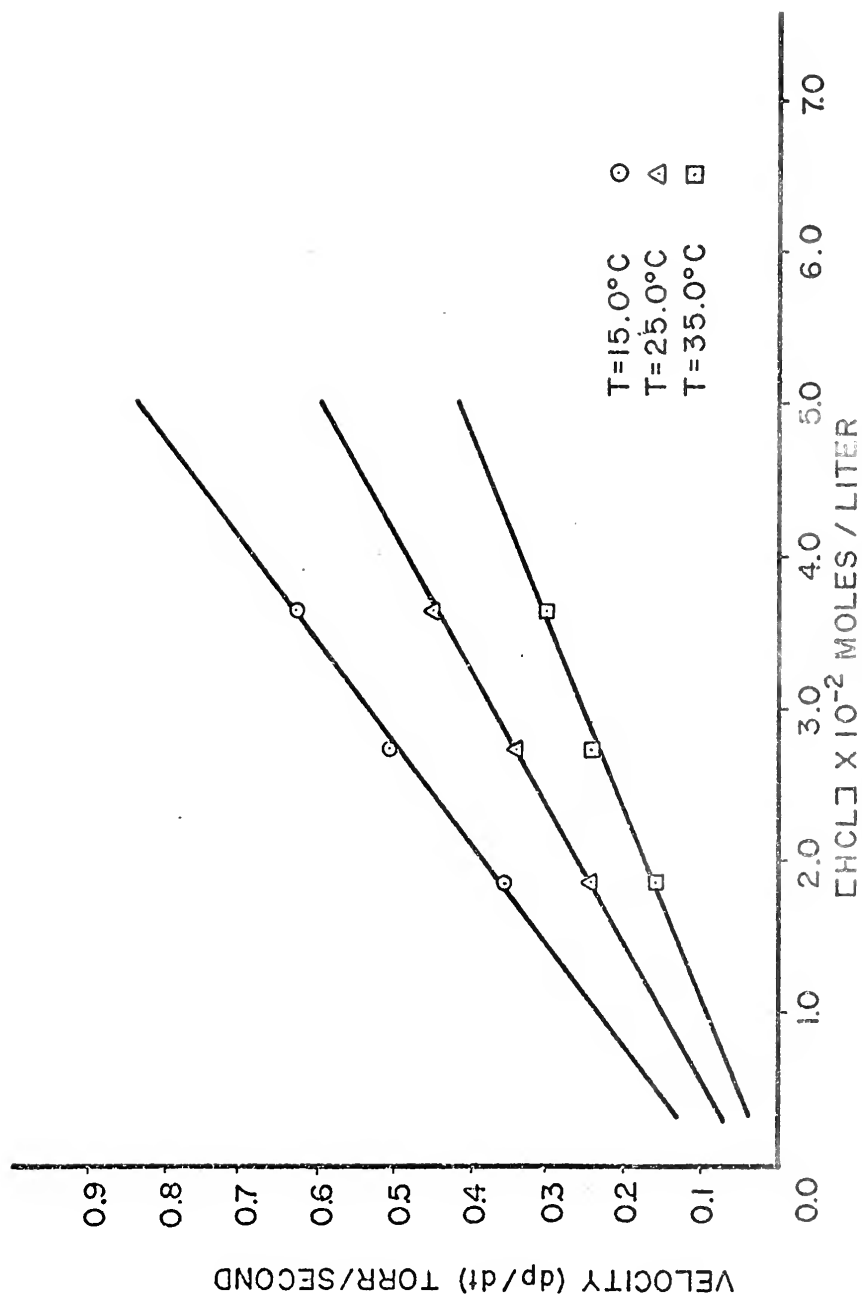
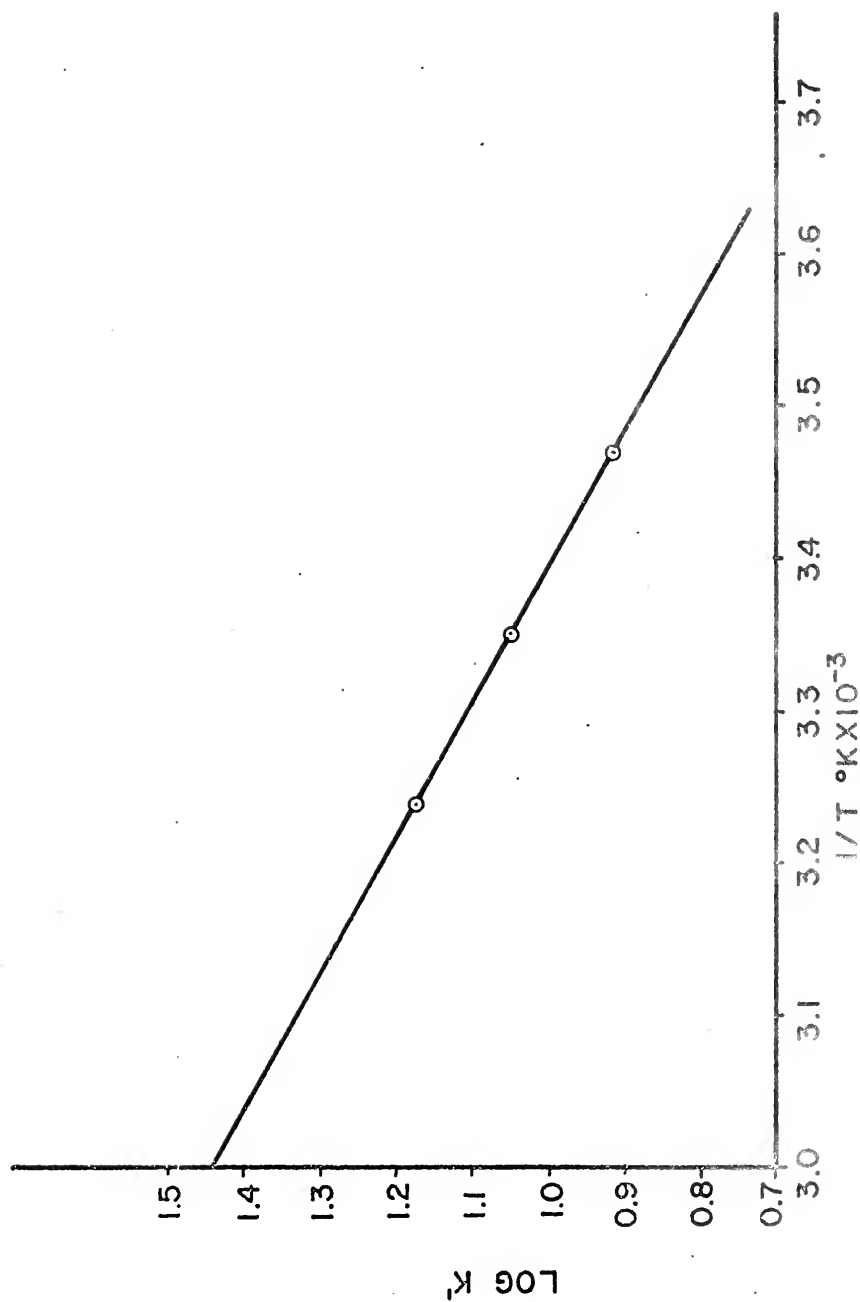


FIG. 4 VELOCITY OF REACTION AT 35.0°C

FIG. 5 DETERMINATION OF RATE CONSTANTS (k')

FIG.6 DETERMINATION OF ACTIVATION ENERGY (E_g)

APPENDIX B

APPENDIX B

Derivation of Relationship Between k' and k

The apparent rate constant, k' , is the slope of the plot of the reaction velocity vs. the concentration of HCl,

$$v = dp/dt = k' [H^+] \quad (3).$$

The true rate constant is defined by

$$dn_{CO_2}/dt = kS [H^+] \quad (5)$$

where n_{CO_2} is the moles of CO_2 evolved during the reaction. The relationship between the two can be derived as follows.

If the simple gas law is assumed to apply to all gases in the system, then at the start of the run, just after the system has been closed to the atmosphere

$$p_0 V_0 = n_a RT \quad (B1)$$

where p_0 is the pressure in the gas phase above the reactants at time zero, i.e. atmospheric, V_0 is the volume of gas (air) in the system at time zero, n_a is the moles of air making up this volume, R is the gas constant, and T is the temperature.

As CO_2 is evolved by the reaction the pressure in the system increases and so does the volume of the gas phase by virtue of the fall in the near leg of the manometer. If the head in the manometer is h and the cross sectional area of its bore is a , then the volume of gas at any time

will be $V_0 + ha/2$. The corresponding pressure will be $p_0 + h$. So at any time after the start of the run

$$(p_0 + h)(V_0 + ha/2) = (n_a + n_{CO_2})RT \quad (B2).$$

The variables in time are h and n_{CO_2} . If equation (B2) is differentiated with respect to time,

$$(V_0 + ha/2) dh/dt + (p_0 + h)(a/2) dh/dt = (RT) dn_{CO_2}/dt \quad (B3)$$

or, rearranging

$$(V_0 + p_0 a/2 + ha) dh/dt = (RT) dn_{CO_2}/dt \quad (B4)$$

in which p_0 , a , and h must obviously be in units of length; p_0 must be in terms of the length of a manometric (mercury) column.

The k' to k conversion involves the change from the measured velocity dh/dt to the alternate dn_{CO_2}/dt . So the problem consists of evaluating the term $V_0 + p_0 a/2 + ha$ in equation (B4).

The appropriate dimensions of the apparatus were measured and found to be: $a = 28.27 \text{ mm}^2$; $V_0 = 189 \text{ cc} = 189000 \text{ mm}^3$. A typical barometric pressure for the laboratory was 745 mm Hg. If this is assumed to apply to all runs, and if the further assumption is made that an average value of h at midpoint in the typical run was 20 mm Hg, the pertinent factors can be calculated to be $V_0 = 189000$, $p_0 a/2 = 10530$, and $ha = 565$, all in mm^3 . The term ha is, therefore, only about 0.3% of the sum of the

other two and can be ignored. The sum of V_0 and $p_0 a/2$ is 199530 mm^3 . Inclusion of this value and that of RT for 25°C gives

$$dh/dt = 92900 \, dn_{\text{CO}_2}/dt \quad (\text{B5})$$

where t is in seconds, n is in moles, and h is in mm Hg.

The other term needed for the evaluation of k is the surface area, S , of the solid in the reaction. The crushed marble sample was sieved between the No. 16 and the No. 30 sieves. The average size of the openings of these two sieves is, from the dimensions given in ASTM E 11, 0.08928 cm . If a cubical model of dimension d is assumed, the specific surface will be $6/d$ in units of reciprocal length. If this value is divided by the density, 2.71 g/cm^3 for calcite, the specific surface in units of cm^2/g is determined to be 24.8 . A sample weight of 2.5 g was used in each run, so the total surface area, S , was 62.0 cm^2 .

When this value is incorporated into equation (5) and combined with equations (3) and (B5), the final relationship between k' and k becomes

$$k = 1.736 \times 10^{-7} k' \quad (\text{B6})$$

where k' is in torr-lit/mole-sec and k is in lit/sec- cm^2 .

As an example, the apparent rate constant for the control reaction at 25°C is $k' = 11.43 \text{ torr-lit/mole-sec}$ (Table 4); therefore the true rate constant is $k = 1.736 \times 10^{-7} \times 11.43 = 1.99 \times 10^{-6} \text{ lit/sec-cm}^2$.



APPENDIX C

APPENDIX C

Calculation of Decrease in Acidity During a Run

According to equation (B5) the relationship between the head developed during a run, Δh , and the moles of CO_2 evolved, Δn_{CO_2} , is

$$\Delta h = 92900 \Delta n_{\text{CO}_2} \quad (\text{C1}).$$

As a typical example, for the control run at 25°C with an initial acid concentration of 0.0364M , Δh at the end of the run was 40 torr. Therefore $n_{\text{CO}_2} = 4.306 \times 10^{-4}$ moles. Twice this value, or 8.611×10^{-4} , is the number of moles of HCl consumed in the reaction. The original 400 ml. of acid contained $0.0364 \times 0.4 = 0.01456$ moles of acid. The amount consumed was, therefore, 5.9% of the original amount. The average concentration of the acid during the run was, therefore, 0.0353M .

A similar calculation for the 25°C control run with an initial acid concentration of 0.0184M shows a 10.2% reduction during the run and an average concentration of 0.0175M .

